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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Dentifrices

We, UNILEVER LIMITED, a Company registered under the laws of Great Britain, of Port Sunlight, in the County of Chester, England do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to dentifrices, and more particularly to 'fluoride' dentifrices, that is, those containing a water-soluble fluorine-containing compound which yields fluoride ions (F^-) in aqueous solution. Such fluorine-containing compounds are incorporated in dentifrices because fluoride ions are able to confer on tooth enamel some resistance to dissolution by the acids generated in the mouth during degradation of food debris.

It is well known that fluoride dentifrices generally have a lower capacity to reduce enamel solubility than one would predict for them, owing to the partial inactivation of the fluoride by the polishing agent of the dentifrice; and it is also known that the extent of inactivation depends very much on the nature of the particular polishing agent employed.

The present invention is concerned with improving the capacity of fluoride dentifrices to reduce enamel solubility, and arises from work we have carried out to investigate what changes in pH occur when fluoride dentifrices are diluted under conditions similar to those prevailing during actual use (as distinct from when they are diluted merely with water), and what capacity to reduce enamel solubility fluoride dentifrices have under those conditions of dilution. Our findings are illustrated in Tables I, II and III. The columns in these tables set out the composition of particular fluoride dentifrices, among which are dentifrices prepared following generally the proposals in British Specification No. 821,925 and in British Specification No. 845,611; and at the foot of each column are shown

(a) the pH (measured by a standard pH meter) at 25°C, of a slurry of one part by weight of the dentifrice and three parts by weight of distilled water

(b) the pH (measured by a standard pH meter) at 25°C, of a slurry of one part by weight of the dentifrice and three parts by weight of a simulated saliva composition (an aqueous solution of the inorganic components of saliva) composed of 1.01 grams pere litre of sodium bicarbonate and 0.71 gram per litre of disodium orthophosphate, adjusted to pH 7.8 by the addition of N-hydrochloric acid

(c) reduction in enamel solubility, as defined by $100(x-y)/x$, where
x = amount of calcium dissolved from unit weight of tooth enamel when the enamel is subjected for 20 minutes to the action of an acid solution buffered to pH 4; and
y = amount of calcium dissolved per unit weight of tooth enamel which, prior to subjection to the acid solution buffered to pH 4, has been treated for 1 hour with the slurry specified in (b).

TABLE I

Ingredient	Example	% by weight 1	2	3	4
Calcium pyrophosphate		—	—	39.0	44.77
Hydrated alumina		—	49.6	—	—
Silica		9.5	2.0	—	—
Sodium carboxymethylcellulose		—	—	1.2	—
Irish moss derivative		0.6	0.9	—	1.3
Humectant		34.96	25.47	30.0	27.0
Magnesium aluminium silicate		—	—	0.4	—
Stannous fluoride		0.41	0.41	0.4	0.41
Stannous pyrophosphate		—	—	1.0	1.0
30% aqueous NaOH solution		0.6	—	—	0.16
Sodium lauryl sulphate		1.26	1.5	0.7	1.26
Sodium coconut monoglyceride sulphonate		—	—	0.81	—
Flavour		0.8	0.9	—	0.9
Saccharin		0.2	0.22	—	0.2
Water, to 100					
pH of dentifrice slurry in water, as in (a)		4.9	4.7	5.0	4.7
pH of dentifrice slurry in simulated saliva, as in (b)		7.1	7.4	6.5	6.1
Reduction in enamel solubility, as in (c)		19%	10%	11%	20%

TABLE II

Ingredient / Example	% by weight 5	6	7	8
Water-insoluble sodium metaphosphate	45.85	46.1	26.23	42.09
$CaHPO_4.2H_2O$	—	—	26.23	—
Anhydrous $CaHPO_4$	5.0	5.0	—	4.0
Sodium carboxymethylcellulose	0.8	0.8	—	—
Irish moss derivative	—	—	—	1.3
Gum tragacanth	—	—	1.44	—
Humectant	29.4	29.4	19.98	26.74
Titanium dioxide	0.4	0.4	—	—
Sodium fluoride	0.2	—	0.22	—
Stannous fluoride	—	0.4	—	0.41
Citric acid	0.25	—	—	—
30% aqueous NaOH solution	—	—	—	0.2
NaH_2PO_4	—	—	0.34	—
Na_2HPO_4	—	—	0.13	—
Sodium benzoate	0.5	0.5	—	—
Sodium lauryl sulphate	—	—	1.16	1.26
Sodium N-lauroyl sarcoside	2.0	2.0	—	—
Flavour	1.0	0.9	0.9	0.9
Saccharin	0.2	0.2	0.2	0.2
Water, to 100				
pH of dentifrice slurry in water, as in (a)	5.5	5.6	6.6	4.8
pH of dentifrice slurry in simulated saliva, as in (b)	7.0	6.4	6.8	6.3
Reduction in enamel solubility, as in (c)	16%	16%	16%	19%

TABLE III

Ingredient	Example	% by weight 9	10	11
Water-insoluble sodium metaphosphate		25.85	42.24	34.0
Calcium pyrophosphate		25.85	5.0	5.0
Sodium carboxymethylcellulose		—	—	1.2
Irish moss derivative		—	1.3	—
Gum tragacanth		1.44	—	—
Humectant		20.38	26.1	28.2
Magnesium aluminium silicate		—	—	0.4
Sodium fluoride		0.22	—	—
Stannous fluoride		—	0.41	0.4
Stannous pyrophosphate		—	—	1.0
30% aqueous NaOH solution		—	0.1	—
Hexachlorophene		—	0.05	—
Sodium lauryl sulphate		1.16	1.26	0.7
Sodium coconut monoglyceride sulphonate		—	—	0.8
Flavour		0.9	0.9	0.9
Saccharin		0.2	0.2	0.1
Water, to 100				
pH of dentifrice slurry in water, as in (a)		5.8	5.3	4.7
pH of dentifrice slurry in simulated saliva, as in (b)		6.5	6.8	6.4
Reduction of enamel solubility, as in (c)		20%	20%	21%

We have now found that the capacity of a fluoride dentifrice to reduce enamel solubility when applied under dilution conditions similar to those prevailing during actual use can be improved by incorporating in it a buffering agent so that, when the pH of a slurry of the dentifrice is measured under the conditions set out earlier in (b), the pH is from 5.0 to 6.0, and preferably from 5.3 to 5.7.

Suitable buffering agents for use in carrying out the invention are water-soluble systems which, in general known *per se*, usually comprise a mixture of a substance which contains replaceable hydrogen and is weakly acidic in reaction and an alkaline-reacting alkali metal salt thereof; for example, the system NaH_2PO_4/Na_2HPO_4, and the system weak organic acid/alkali metal salt thereof. Examples of the latter are: acetic acid/sodium acetate; malic acid/sodium malate; and sorbic acid/sodium sorbate.

Embodiments of the invention are set out in Tables IV and V. These tables illustrate the application of the invention to dentifrices based on polishing agents as follows:

Example	Polishing Agent
12	Silica; for improvement in reduction of enamel solubility, compare with Example 1
13	A mixture of hydrated alumina and silica; for improvement in reduction of enamel solubility, compare with Example 2
14	Calcium pyrophosphate; for improvement in reduction of enamel solubility, compare with Examples 3 and 4
15	A mixture of a water-insoluble sodium metaphosphate with up to its own weight of dicalcium ortho phosphate; for improvement in reduction of enamel solubility, compare with Examples 5 to 8
16 to 21	A mixture of a water-insoluble sodium metaphosphate with up to its own weight of calcium pyrophosphate; for improvement in reduction of enamel solubility, compare Example 16 with 9, Examples 17 to 20 with 10, and Example 21 with 11

TABLE IV

Ingredient	% by weight		
Example	12	13	14
Calcium pyrophosphate	—	—	43.29
Hydrated alumina	—	47.1	—
Silica	7.92	2.0	—
Irish moss derivative	0.6	0.9	1.3
Humectant	33.81	23.45	26.34
Stannous fluoride	0.41	0.41	0.41
Stannous pyrophosphate	—	—	1.0
Sorbic acid	5.0	5.0	1.5
30% aqueous NaOH solution	1.5	1.5	1.4
Sodium lauryl sulphate	1.26	1.5	1.26
Flavour	0.8	0.9	0.9
Saccharin	0.2	0.2	0.2
Water, to 100			
pH of dentifrice slurry in water, as in (a)	4.8	4.9	4.8
pH of dentifrice slurry in simulated saliva, as in (b)	5.0	5.0	5.5
Reduction in enamel solubility, as in (c)	29%	27%	27%

TABLE V

Ingredient	Example	% by weight 15	16	17	18	19	20	21
Water-insoluble sodium metaphosphate		37.29	25.35	36.75	40.21	40.09	40.19	32.5
Calcium pyrophosphate		—	25.35	5.0	5.0	5.0	5.0	5.0
Anhydrous $CaHPO_4$		4.0	—	—	—	—	—	—
*Binding Agent		1.3	1.43	1.3	1.1	1.1	1.3	1.2
Humectant		26.74	18.8	33.89	29.19	33.89	26.25	27.78
Magnesium aluminium silicate		—	—	—	—	—	—	0.4
Sodium fluoride		—	0.22	—	—	—	—	—
Stannous fluoride		0.41	—	0.42	0.41	0.41	0.41	0.4
Stannous pyrophosphate		—	—	—	—	—	—	1.0
Malic acid		—	—	2.0	—	—	—	—
Sorbic acid		4.0	1.5	—	—	—	1.5	1.5
Acetic acid		—	—	—	—	0.8	—	—
30% aqueous NaOH solution		1.0	0.8	3.63	—	1.8	0.8	1.0
NaH_2PO_4		—	—	—	0.86	—	—	—
Na_2HPO_4		—	—	—	1.19	—	—	—
Hexachlorophene		—	—	—	—	—	0.05	—
Benzoic acid		—	—	—	0.08	—	—	—
Sodium lauryl sulphate		1.26	1.16	1.26	1.26	1.26	1.26	‡1.5
Flavour		0.9	0.9	0.9	0.9	0.7	0.75	0.9
Saccharin		0.2	0.2	0.2	0.13	0.1	0.2	0.1
Water, to 100								
pH of dentifrice slurry in water, as in (a)		4.9	5.2	5.2	5.3	5.3	5.0	4.7
pH of dentifrice slurry in simulated saliva, as in (b)		5.2	5.5	5.5	5.7	5.7	5.3	5.2
Reduction of enamel solubility as in (c)		30%	34%	34%	35%	41%	42%	38%

* Irish moss derivative in Examples 15 and 17 to 20; gum tragacanth in Example 16; and sodium carboxymethylcellulose in Example 21.

‡ 0.7 sodium lauryl sulphate + 0.8 sodium coconut monoglyceride sulphonate.

The composition of the buffering agent, and the proportion of it employed in the dentifrice, are chosen so that the pH of a slurry of the dentifrice when measured under the conditions specified earlier in (b) is from 5 to 6. Merely to include a buffering agent, without regard to this particular pH, is not in accordance with the invention; thus, the dentifrice of Example 7 in Table II, where the system NaH_2PO_4/Na_2HPO_4 is present but the relevent pH is considerably above 6 (in fact, it is 6.8), is not one in accordance with the invention. In general, the amount of buffering agent employed forms from 0.02 to 10%, and preferably from 0.1 to 2%, by weight of the dentifrice. As will be seen from Examples 12 to 21, the rise in pH that is observed when water as diluent is replaced by simulated saliva is, in all these Examples, not greater than 1; and only in Example 14 is it greater than 0.5.

Examples of fluorine-containing compounds which may be present in the dentifrice are sodium, potassium, lithium, ammonium, geranium, aluminium and stannous fluorides, and stannous chlorofluoride. The compounds are ordinarily used in an amount capable of supplying fluoride ions (F^-) in amounts forming from 0.01 to 2%, and preferably from 0.05 to 0.25, by weight of the dentifrice.

The dentifrice can contain as little as 7% by weight of polishing agent, but it preferably contains from 20 to 80% by weight thereof. If the dentifrice is in a paste form (as distinct from powder form), the polishing agent preferably forms from 40 to 60% by weight of it.

According to a preferred feature of the invention, the polishing agent employed comprises from 50 to 99% by weight of a water-insoluble sodium metaphosphate and from 1 to 50% by weight of calcium pyrophosphate, dicalcium orthophosphate, silica or alumina. A polishing agent which comprises from 80 to 98% by weight of a water-insoluble sodium metaphosphate and from 2 to 20% by weight of calcium pyrophosphate is particularly preferred. A synthetic organic polymer can also be used as polishing agent.

The dentifrice may contain a germicide, such as 2,2¹-methylene-bis(3,4,6-trichlorophenol) which is sold under the name 'Hexachlorophene,' 3,4¹,5-tribromosalicylanilide and 3,4,4¹-trichlorocarbanilide. Such a germicide is preferably present in an amount forming from 0.01 to 2%, and preferably in an amount from 0.03 to 0.2%, by weight of the dentifrice. The dentifrice of Example 20, which contains hexachlorophene as germicide and sorbic acid/sodium sorbate as buffering agent, has especially good effectiveness against Staphylococcus aureus.

WHAT WE CLAIM IS:—

1. A dentrifice comprising a polishing agent and a water-soluble fluorine-containing compound which yields fluoride ions in aqueous solution, and including a buffering agent, the dentifrice being such that, when the pH of a slurry of the dentifrice is measured under the conditions set out in (b) herein, the pH is from 5 to 6.

2. A dentifrice according to Claim 1, being such that the pH specified is from 5.3 to 5.7.

3. A dentifrice according to Claim 1 or 2, in which the buffering agent is a mixture of a weak organic acid and an alkali metal salt thereof.

4. A dentifrice according to Claim 3, in which the buffering agent is a mixture of acetic acid and alkali metal acetate.

5. A dentifrice according to Claim 3, in which the buffering agent is a mixture of sorbic acid and alkali metal sorbate.

6. A dentifrice according to Claim 3, in which the buffering agent is a mixture of malic acid and alkali metal malate.

7. A dentifrice according to Claim 1 or 2, in which the buffering agent is a mixture of mono-sodium and di-sodium orthophosphates.

8. A dentifrice according to any one of Claims 1 to 7, in which the difference between the pH of a slurry of the dentifrice when measured under conditions (b) herein and the pH of a slurry of the dentifrice when measured under conditions (a) herein, is not greater than 0.5.

9. A dentifrice according to any one of Claims 1 to 7, in which, when the pH of a slurry of the dentifrice is measured under the conditions set out in (a) herein, the pH is at least 4.7.

10. A dentifrice according to any one of Claims 1 to 9, in which the buffering agent forms from 0.02 to 10% by weight of the dentifrice.

11. A dentifrice according to Claim 10, in which the buffering agent forms from 0.1 to 2% by weight of the dentifrice.

12. A dentifrice according to any one of Claims 1 to 11, in which the polishing agent forms from 7 to 80% by weight of the dentifrice.

13. A dentifrice according to Claim 12, in which the polishing agent forms from 20 to 80% by weight of the dentifrice.

14. A dentifrice according to Claim 13, in which the polishing agent forms from 40 to 60% by weight of the dentifrice.

15. A dentifrice according to any one of Claims 1 to 14, in which the polishing agent is calcium pyrophosphate.

16. A dentifrice according to any one of Claims 1 to 14, in which the polishing agent is silica.

17. A dentifrice according to any one of Claims 1 to 14, in which the polishing agent is a mixture of alumina and silica.

18. A dentifrice according to any one of Claims 1 to 14, in which the polishing agent comprises from 50 to 99% by weight of a water-insoluble sodium metaphosphate and

from 1 to 50% by weight of calcium pyrophosphate.

19. A dentifrice according to Claim 18, in which the polishing agent comprises from 80 to 98% by weight of a water-insoluble sodium metaphosphate and from 2 to 20% by weight of calcium pyrophosphate.

20. A dentifrice according to any one of Claims 1 to 14, in which the polishing agent comprises from 50 to 99% of a water-insoluble sodium metaphosphate and from 1 to 50% by weight of di-calcium orthaphosphate.

21. A dentifrice according to any one of Claims 1 to 14, in which the polishing agent comprises from 50 to 99% by weight of a water-insoluble sodium metaphosphate and from 1 to 50% by weight of silica or alumina.

22. A dentifrice according to any one of Claims 1 to 21, in which the water-soluble fluorine-containing compound is stannous fluoride.

23. A dentifrice according to any one of Claims 1 to 21, in which the water-soluble fluorine-containing compound is sodium fluoride.

24. A dentifrice according to any one of Claims 1 to 23, in which the water-soluble fluorine-containing compound is present in an amount capable of supplying fluoride ions in amounts forming from 0.01 to 2% by weight of the dentifrice.

25. A dentifrice according tc Claim 24, in which the water-soluble fluorine-containing compound is present in an amount capable of supplying fluoride ions in amounts forming from 0.05 to 0.25% by weight of the dentifrice.

26. A dentifrice according to any one of the preceding claims, which contains the germicide 2,2'-methylene-bis(3,4,6-trichlorophenol).

27. A dentifrice substantially as described in Example 12, 13 or 14.

28. A dentifrice substantially as described in Example 15.

29. A dentifrice substantially as described in Example 16, 17, 18, 19 or 20.

30. A dentifrice substantially as described in Example 21.

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